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13. ABSTRACT (Maximum 200 words) The utility of a permanent magnet is in many applications determined by its maximum energy product, $(BH)_{max}$. This is the maximum value of the product of B and H in the 2nd quadrant of the hysteresis loop. The amount of magnetic material to meet a certain need is inversely related to $(BH)_{max}$. If size of a device is controlled by the volume of magnetic material needed, it is clear that one may downsize the device by using a higher energy product material.
High energy permanent magnets find utility in many devices - TWT's, klystrons, linear induction accelerators, etc., as well as electric motors and generators. At present there are only 3 permanent magnet materials in widespread use - $SmCo_5$, $Nd_2Fe_{14}B$ and $SmCo_5$-Sm_2Co_{17}. Each has weakness. The present study sought to find new and better materials. The findings in this work are described in detail in 33 journal publications. About a third of the effort has been devoted to effecting improvements in existing materials which occur in the $SmCo_5$ or $Nd_2Fe_{14}B$ structures. Materials forming in the $ThMn_{12}$ and $LaCo_{13}$ structures were also studied. About half of the effort was devoted to developing a preparation scheme to form $Fe_{16}N_2$, which is reported to have a theoretical energy product of ~200 MGOe. $Fe_{16}N_2$ has been formed but in the presence of large amounts of α Fe and γ Fe-N alloy. The enlarged B value reported for $Fe_{16}N_2$ has been confirmed in the present study.

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STUDIES DIRECTED TOWARD NEW AND IMPROVED PERMANENT MAGNET MATERIALS

FINAL REPORT

by

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ABSTRACT

The utility of a permanent magnet is in many applications determined by its maximum energy product, $(BH)_{max}$. This is the maximum value of the product of B and H in the 2nd quadrant of the hysteresis loop. The amount of magnetic material to meet a certain need is inversely related to $(BH)_{max}$. If size of a device is controlled by the volume of magnetic material needed, it is clear that one may downsize the device by using a higher energy product material.

High energy permanent magnets find utility in many devices - TWT's, klystrons, linear induction accelerators, etc., as well as electric motors and generators. At present there are only 3 permanent magnet materials in widespread use - $SmCo_5$, $Nd_2Fe_{14}B$ and $SmCo_5$-Sm_2Co_{17}. Each has weakness. The present study sought to find new and better materials. Findings in the work are described in detail in 33 journal publications. About a third of the effort has been devoted to effecting improvements in existing materials which occur in the $SmCo_5$ or $Nd_2Fe_{14}B$ structures. Materials forming in the $ThMn_{12}$ and $LaCo_{13}$ structures were also studied. About half of the effort was devoted to developing a preparation scheme to form $Fe_{16}N_2$, which is reported to have a theoretical energy product of $\sim$ 200 MGOe. $Fe_{16}N_2$ has been formed but in the presence of large amounts of α Fe and γ' Fe-N alloy. The enlarged B value reported for $Fe_{16}N_2$ has been confirmed in the present study.

I. INTRODUCTION

This report is concerned with a series of studies carried out in the three-year period ending August 31, 1994 dealing with materials needed to fabricate high energy permanent magnets. High energy magnets at present are invariably rare earth alloy magnets. These have replaced ferrite or alnico magnets for many applications. The rare earth magnets represent a revolutionary development in that they permit magnet energy densities an order of magnitude or more higher than that provided by the alnicos and ferrites. The Army Research Office has played a significant role in opening up this area of new and useful materials.

In large measure the utility of a permanent magnet is defined by its so-called maximum energy product. The maximum energy product is the maximum value of the product of B and H in the 2nd quadrant of the magnetic hysteresis loop, viz., $(BH)_{max}$. The values for $(BH)_{max}$ reach 4 MGOe for Ba ferrite magnets and 6 MGOe for alnico 5. In contrast, a $(BH)_{max}$ value of 52 MGOe has been achieved with the rare earth-containing magnets which are comprised of $Nd_2Fe_{14}B$.

The quantity of magnetic material needed for a specific application is inversely related to the energy product of the material used to form the magnet. The major significance of high energy magnetic materials is that they permit devices to be downsized. High energy magnets permit downsizing of motors, generators and linear actuators. This feature is of significance in both military and civilian applications. High energy permanent magnets are used not only in electromechanical devices

but also in computer peripherals (disk drives), electronic equipment (travelling wave tubes for generating microwaves, etc.), wigglers and undulators employed to enhance synchrotron radiation, etc.

Conventional commercial magnets are exhibited by an energy product of 35 MGOe or less, whereas the highest energy laboratory magnets are, as indicated above, 52 MGOe magnets. Very much higher energies are potentially available - up to 350 MGOe for some of the pure elemental rare earths and in excess of 200 MGOe for 3d transition metal alloys and compounds. From present-day knowledge of their intrinsic magnetic characteristics, the potential high energy of the elemental rare earths seems to be beyond reach. However, there is the possibility that the high energies of the 3d transition metal systems may be realized. This will require improvement in our knowledge and understanding of coercivity in such systems and the utilization of this improved understanding to control coercivity.

To obtain a high maximum energy product it is necessary that the magnetic material have a large magnetic induction (B) in the 2nd quadrant of the hysteresis loop. Retaining a large value of the magnetic induction (B) in the 2nd quadrant of the hysteresis loop necessitates that the material exist in a metastable state. Experience shows that impurities of the kind which are normally in magnetic materials results in the rapid relaxation of the metastable material to the stable state. Under such circumstances the material has little or no coercive force. It is a soft material, has a small value of B in the 2nd quadrant, and has a negligible energy product. If we can arrange matters so as to prevent

this rapid relaxation, we have a high coercivity (H_c) and a hard magnetic material. If we simultaneously have a large remanence (B_r), we have a high energy magnet material. Hence, the quest for a high energy magnet material consists in finding a material which has simultaneously a large B_r and a large H_c. Finding materials with a large B_r is not difficult. To find materials which have a large B_r AND a large H_c is very difficult. Prior to 1983 only one such material was known: $SmCo_5$. In late 1983, $Nd_2Fe_{14}B$ was identified as a second high energy magnet material.[1] These two materials currently are worldwide items of commerce. These are very useful magnetic materials, but each has limitations.

$SmCo_5$ has a low theoretical energy product - 31 MGOe. The actual energy product obtained for this material has never exceeded 28.6 MGOe. In contrast, $Nd_2Fe_{14}B$, as noted above, has been used to produce magnets with 52 MGOe energy product. However, $Nd_2Fe_{14}B$ is corrosion-susceptible and has a Curie temperature about 500 C lower than that of $SmCo_5$. Thus, $Nd_2Fe_{14}B$ is of very limited utility at high temperatures and in corrosive environments. Under these circumstances, $SmCo_5$ is the material of choice, this despite its low energy.

The main objectives of the work carried out in Grant No. DAAL03-91-G-0027 were three-fold: (1) To synthesize and characterize magnetically the nitrides of Fe since one of these nitrides, viz., $Fe_{16}N_2$, reputedly has a moment significantly enhanced relative to elemental Fe; (2) To improve the energy product of the so-called 2:17 magnets and (3) To continue the search for new and, hopefully, better magnetic materials.

II. MILITARY SIGNIFICANCE OF PERMANENT MAGNETS

The significance of magnetic materials has been alluded to in the preceding section, but only briefly. In this section some additional details are given, including some examples of the military utility of high performance magnets. Most military applications can be grouped into two categories: (1) those in which the magnet generates a force influencing the motion of an object of macroscopic dimensions and (2) electronic devices in which a magnet generates a field that affects the motion of a stream of electrons. In the latter category are devices which generate beams of microwaves [travelling wave tubes, klystrons, gyrotrons, etc.], linear induction accelerators, high-power free electron lasers, etc. The first category includes all electromechanical force devices - linear actuators, motors, generators, stepper motors, disk drives, voice coil motors, torque couplers, etc.

Often, military applications require the highest level of performance. The high energy magnets being developed in the present program are directed toward meeting these needs. As an example, $SmCo_5$-Sm_2Co_{17} composites are used in travelling wave tubes (TWT) fabication. TWTs generate microwaves that are needed for tracking and communication, both of vital significance in military technology. The composites normally used to fabricate TWTs have energy products in the range of 15-18 MGOe. In these materials, which are doped with Fe, Cu, Zr and certain of the heavy rare earths, the energy product falls far short of what is possible and TWT performance suffers accordingly. In the program at Carnegie Mellon University, other

formulations have been explored and the foundation is being laid for substantial improvement in the magnets used in TWT fabrication. This will in turn lead to improved devices for high-power microwave generation.

In the permanent magnet field there are two major needs: (1) high energy magnets, which will permit downsizing and miniaturization of motors, generators and actuators and (2) cheaper magnets, even ones with modest energy projects - in the range of 10 MGOe. If cost can be sufficiently reduced, magnets in the latter category will supplant ferrites in a wide range of electromechanical devices and will result in improved performance of those devices. There is obvious utility of high energy magnets in that they permit one to fabricate very compact high torque motors and significantly downsized generators. The high energy magnets represent a step up the magnetic energy density ladder toward that provided by superconductor electromagnets. The permanent magnets offer the advantage that they perform at room temperature and above. In contrast, superconductor magnets entail liquid helium temperatures. Superconductors operating at room temperature remain at present only a distant dream.

III. RESUMÉ OF MOST RECENT ACCOMPLISHMENTS

A detailed account of the new and significant accomplishments is given in the 33 published papers listed in Table 1. Two of these (Nos. 27 and 28) are review papers which consolidate and integrate the results of studies of high energy magnets in the program at Carnegie Mellon University and corresponding programs in laboratories throughout the world. (Actually, Nos. 1 and 12 are also review papers.) Two of the

publications (Nos. 8 and 9) deal with the scientifically interesting and industrially important 2:17 systems. We are considering further studies on 2:17 systems, and these investigations have helped lay the groundwork for 2:17 studies which may be made in the future. Whether or not there is extension of this work is contingent upon whether or not there is rising commercial interest in 2:17 materials.

Five studies (Nos. 22-26) are contributions to expand our understanding of 3-, 4- and 5-component systems which occur in the $ThMn_{12}$ structure. These $ThMn_{12}$ structure materials are potentially useful magnetic substances. Six studies (Nos. 13-18) deal with nitrogenated R_2Fe_{17} systems. These materials are attracting massive attention since it was discovered[2,3] a few years ago that nitrogenation improves the intrinsic magnetic properties (moment, T_C and uniaxial anisotropy) of Sm_2Fe_{17}, which is otherwise useless. Ten of the studies (Nos. 1-10) involve $R_2Fe_{14}B$ or $R_2Co_{14}B$-based systems, and three involve $PrCo_5$-based systems (Nos. 19-21). These are studies carried out to effect incremental improvement in $Nd_2Fe_{14}B$- and $PrCo_5$-based systems. Five studies (Nos. 29-33) deal with a variety of magnetic alloy systems.

Reprints of all of these papers except No. 12 have been sent to the ARO.

IV. SOME HIGHLIGHTS OF THE STUDIES

The details of the results of the work carried out in the contract period ending August 31, 1994 are described in the 33 publications

TABLE 1

Published Papers Emanating from the Program

April 1, 1990 - August 31, 1994

$R_2Fe_{14}B$ or $R_2Fe_{14}B$-Based Alloys

1. W. E. Wallace, Janean M. Elbicki and J. G. Sohn, "High Energy Magnets and Other Related Rare Earth Systems," in Recent Advances in Magnetism and Magnetic Materials, H. L. Huang and P. C. Kuo, World Scientific Publications, Singapore (1990), p. 154.

2. F. Pourarian, S. Simizu, R. T. Obermyer, S. G. Sankar and W. E. Wallace, "High Field Magnetic Behavior of $Pr_{15}Fe_{63}Co_{16}GaB_5$ Sintered Magnet," Proc. of 11th Int'l. Workshop on Rare Earth Magnets and Their Applications, S. G. Sankar, ed., Vol. I, p. 401 (1990).

3. L. Y. Zhang, Meiqing Huang and W. E. Wallace, "Magnetic and Structural Characteristics of the $Cfmm_2Fe_{14-x}Co_xB$ System (Cfmm = Ce-free Mischmetal),: J. Mag. Magn. Mat. 103, 245 (1992).

4. M. Q. Huang, L. Y. Zhang, J. M. Elbicki and W. E. Wallace, "Nd-Fe-B Permanent Magnets Doped with Ce-free Misch Metal, Dy, Al, Nb, V or Ga," Proc. of the 12th Int'l. Workshop on Rare Earth Magnets and Their Applications, published by Univ. of Western Australia, Perth, R. Street, Ed. (1992), p. 516.

5. L. Y. Zhang, E. B. Boltich and W. E. Wallace, "Spin Reorientations in the $Cfmm_2Fe_{14-x}Co_xB$ Systems," J. Magn. Magn. Mat. 111, 75 (1992).

6. C. N. Christodoulou, T. B. Massalski and W. E. Wallace, "Magnetic Hardening of the $Pr_2Co_{14}B$-based Rapidly Quenched Alloys," J. Mag. Magn. Mat. 125, 177 (1993).

7. F. Pourarian, R. Obermyer, Y. Zheng, S. G. Sankar and W. E. Wallace, "Crystal Structure and Magnetic Characteristics of Alloys Based on R-Fe-Si (R = Y,Nd,Gd,Dy,Ho,Er)," J. Appl. Phys. 73, 6272 (1993)

2:17 Systems

8. M. Q. Huang, Y. Zheng, J. G. Sohn, J. M. Elbicki, W. E. Wallace and S. G. Sankar, "Al, Ga Substitution in 2:17 Type Magnets with High Fe Content," Proc. of 11th Int'l. Workshop on Rare Earth Magnets and Their Applications, S. G. Sankar, ed., Vol. I, p. 457 (1990).

9. M. Q. Huang, Y. Zheng and W. E. Wallace, "SmCo (2:17 Type) Magnets with High Contents of Fe and LRE," J. Appl. Phys. 75, 6280 (1994).

Table 1 (cont.)

FeN Alloys

10. M. Q. Huang, W. E. Wallace, S. Simizu, R. T. Obermyer and S. G. Sankar, "Synthesis and Characterization of $Fe_{16}N_2$ in Bulk Form," J. Appl. Phys. 75, 6574 (1994).

11. M. Q. Huang, W. E. Wallace, S. Simizu and S. G. Sankar, "Magnetism of α' Fe and α" Fe Nitrides," J. Mag. Magn. Mat. 135, 226 (1994).

12. W. E. Wallace and M. Q. Huang, "Enhanced Fe Moment in Nitrogen Martensite and $Fe_{16}N_2$," accepted for publication.

Nitrogenated $R_2(Co,Fe)_{17}$ Systems

13. M. Q, Huang, B. M. Ma, W. E. Wallace and S. G. Sankar, "Magnetic Properties and Structure of Nitrogenated $R_2(Fe,Co)_{17}$ Intermetallic Compounds," Proc. of 11th Int'l. Workshop on Rare Earth Magnets and Their Applications, S. G. Sankar, ed., Vol. II, p. 204 (1990).

14. L. Y. Zhang, Y. Zheng and W. E. Wallace, "Magnetization and PCIs of Nitrogenated $R_2(Co_xFe_{1-x})_{17}$ Systems," ibid., Vol. II, p. 219 (1990).

15. M. Q. Huang, Y. Zheng, K. Miller, J. M. Elbicki and S. G. Sankar, "Magnetism of $(Sm,R)_2Fe_{17}N_y$ (R = Y,Tb or Mischmetal)," J. Appl. Phys. 70, 6024 (1991).

16. M. Q. Huang, L. Y. Zhang, B. M. Ma, Y. Zheng, J. M. Elbicki, W. E. Wallace and S. G. Sankar, "Metal-Bonded Sm_2Fe_{17}-N-Type Magnets," J. Appl. Phys. 69, 6027 (1991).

17. M. Q. Huang, Y. Zheng, K. Miller, J. M. Elbicki, S. G. Sankar, W. E. Wallace and R. Obermyer, "Magnetic Properties of $(Sm_{1-x}R_x)_2Fe_{17}N$ (R = Ce,Nd and Mischmetal)," J. Mag. Magn. Mat. 102, 91 (1991).

18. M. Q. Huang, A. T. Pedziwiatr, F. Pourarian, W. E. Wallace and S. G. Sankar, "Structural and Magnetic Properties of Thermally Stabilized $Sm_2Fe_{17}N_x$ by Silicon Substitution," Proc. of the 7th Int'l. Symposium on Magnetic Anisotropy and Coercivity in Rare Earth-Transition Metal Alloys, published by Univ. of Western Australia, Perth, R. Street, Ed. (1992), p. 301.

Tsble 1 (cont.)

RCo_5-Based Systems

19. Y. Xu, B. M. Ma, W. E. Wallace and S. G. Sankar, "Magnetic Properties of Sintered $(Pr,La)Co_5$-Type Magnets,: Proc. of 11th Int'l. Workshop on Rare Earth Magnets and Their Applications, S. G. Sankar, ed., Vol. I, p. 481 (1990).

20. B. M. Ma, E. B. Boltich, S. G. Sankar, W. E. Wallace, S. K. Malik and C. V. Tomy, "Spin-reorientation Phenomenon in Pseudobinary $(Pr_{1-x}R_x)Co_5$ Compounds (R = Sm,Gd,Dy,Tb,Ho and Er) as Determined by ac Susceptibility Measurements," J. Appl. Phys. 69, 6061 (1991).

21. B. M. Ma, T. Kawai, S. G. Sankar and W. E. Wallace, "An Analysis of the Pr Contribution to the Spin-reorientation Phenomenon in $PrCo_5$," J. Appl. Phys. 70, 6131 (1991).

1:11 Systems Forming in the $ThMn_{12}$ Structure

22. S. F. Cheng, Y. Xu, S. G. Sankar and W. E. Wallace, "Phase Analysis and Magnetic Properties of $RTiFe_{11-x}Co_x$ (R = Pr,Nd)(x = 0-11)," Proc. of 11th Int'l. Workshop on Rare Earth Magnets and Their Applications, S. G. Sankar, ed., Vol. II, p. 400 (1990).

23. S. F. Cheng, B. M. Ma, Y. Zheng, V. K. Sinha, S. G. Sankar and W. E. Wallace, "Investigation of $RTiFe_{11-x}Co_x$ Alloys (R = Tb,Dy,Ho and Er, x = 0-11)," ibid., Vol. II, p. 436 (1990).

24. L. Y. Zhang, S. G. Sankar, W. E. Wallace and S. K. Malik, "Structural and Magnetic Properties of $RTiFe_{11}$ and Their Hydrides (R = Gd,Tb,Dy, Ho and Er)," ibid., Vol. II, p. 493 (1990).

25. S. F. Cheng, V. K. Sinha, B. M. Ma, S. G. Sankar and W. E. Wallace, "Phase Analysis and Magnetic Properties of $RTiFe_{11-x}Co_x$ (R = Y,Gd) (x = 0-11)," J. Appl. Phys. 69, 5599 (1991).

26. L. Y. Zhang, B. M. Ma, Y. Zheng and W. E. Wallace, "Spin-reorientation Phenomena in $(Tb_xEr_{1-x})TiFe_{11}$ Systems," ibid., 6119 (1991).

Reviews

27. W. E. Wallace, "Magnetism of Rare Earth Intermetallics: An Overview," in Rare Earth Resources: Science, Technology and Applications, Renata G. Bautista and Norton Jackson, Eds., TMS Publication, p. 409 (1992).

Table 1 (cont.)

28. W. E. Wallace and M. Q. Huang, "Magnetism of Intermetallic Nitrides: A Review," IEEE Trans. Mag. 28, 2312 (1992).

Other Systems

29. J. M. Elbicki, L. Y. Zhang, R. T. Obermyer, W. E. Wallace and S. G. Sankar, "Magnetic Studies of $(Gd_{1-x}M_x)_5Si_4$ Alloys (M = La or Y)," J. Appl. Phys. 69, 5571 (1991).

30. M. Q. Huang, B. M. Ma, S. F. Cheng and W. E. Wallace, "Magnetic and Structural Characteristics of the $Pr_2(Co,Fe)_7B_3$ System," ibid., 69, 5599 (1991).

31. Y. Xu, J. M. Elbicki, W. E. Wallace, S. Simizu and S. G. Sankar, "Magnetic and Structural Properties of Fe_3GeN_x," IEEE Trans. Mag. 28, 2569 (1992).

32. M. Q. Huang, Y. Zheng, K. Miller, J. Elbicki, W. E. Wallace and S. G. Sankar, "Magnetic Properties and Structure of Nitrogenated $La(Co_{1-x}Fe_x)_{13}$ Compounds (x = 0-0.4)," ibid., 2860 (1992).

33. M. Q. Huang, S. Simizu and W. E. Wallace, "Synthesis and Properties of a Magnetically Hard $(Sm,Fe,Co,Ti)_{17}$ Phase in Sintered Magnets," J. Appl. Phys. 73, 5902 (1993).

listed in Table 1. As noted earlier, copies of these publications have been provided to the ARO as part of the normal reporting procedure. Hence, it seems inappropriate to provide another detailed account. Instead, a few highlights of the work are provided.

A. Improving Coercivity in 2:17 Magnets

One of the stated objectives of the program was to produce 2:17 type magnets with enhanced energy products. The highest energy products obtained[4] to date are 32-34 MGOe, which contrasts sharply with the theoretical limit for $Sm_2(Co,Fe)_{17}$ alloys which can reach 60 MGOe. There are many reasons for this large difference between potential and the laboratory-achieved energies. One of these is the need with commercial magnets for doping with heavy rare earths to achieve temperature stability. This doping lowers B_r quite sharply. 2:17 magnets in commercial use may have energy products lower than 20 MGOe. This should and can be raised. As noted in publication No. 9*, this can be done by raising the Fe content and/or replacing Sm (which is non-magnetic) with Pr (which is strongly magnetic). These dopings raise B_r. Unfortunately, when these compositional changes are made, H_c suffers and no improvements in energy product result from this kind of compositional modification. However, doping this multicomponent alloy with Ga leads to a significant rise in energy product. This comes about by improvements in coercivity. This is consistent with earlier observations[5] which showed that Ga doping is unusually effective in increasing coercivity in a wide range of rare earth-transition element alloys.

*These numbers refer to the number of the publications in Table 1.

B. Effect of Nitrogenation on magnetic Properties of R_2Fe_{17}

In 1990 Coey and Sun showed[2] that Sm_2Fe_{17} absorbs nitrogen under appropriate conditions and with a dramatic improvement in intrinsic magnetic properties. Almost simultaneously, Huang, Ma, Wallace and Sankar showed[3] that R_2Fe_{17} with R = Y and Gd behaved similarly. This was also true for $Sm_2(Fe_{1-x}Co_x)_{17}$, although the effect of nitrogenation is not so dramatic for $Sm_2(Fe_{1-x}Co_x)_{17}$.

Nitrogenation of Y_2Fe_{17}, Gd_2Fe_{17} and $Sm_2(Fe_{1-x}Co_y)_{17}$ systems was investigated by Huang et al. in the temperature range from 573 to 873 K. The optimum nitrogen absorbed in the R_2Fe_{17} system is around 2.5 to 2.7 atoms per formula unit. Lattice parameters and volume expansion all increase with increasing nitrogen content. Experiments show that Sm_2Fe_{17} transforms from planar to axial anisotropy upon nitrogenation. Nitrogenation increases the saturation magnetization at 4.2 K from 34.7 μ_B/f.u. for Y_2Fe_{17} to 40.3 μ_B/f.u. for $Y_2Fe_{17}N_{2.6}$, from 22.9 μ_B/f.u. for Gd_2Fe_{17} to 30.3 μ_B/f.u. for $Gd_2Fe_{17}N_{2.5}$ and from 28.3 μ_B/f.u. for Sm_2Fe_{17} to 35.2 μ_B/f.u. for $Sm_2Fe_{17}N_{2.6}$. It is noted that the increase of the saturation magnetization is less in the Co-containing $Sm_2(FeCo)_{17}$ alloys by a factor of 3.

Nitrogenation generates a significant improvement on the magnetic anisotropy in the $Sm_2(Fe_{1-y}Co_y)_{17}N_x$ system. Magnetic anisotropy alters from planar to axial for y = 0, 0.2 and 0.4 and x = 2.6 to 2.7. The anisotropy field increases from 34 kOe for $Sm_2(Fe_{0.4}Co_{0.6})_{17}$ to 62 kOe for $Sm_2(Fe_{0.4}Co_{0.6})_{17}N_{2.3}$ at 295 K.

The nitride has properties that make it attractive for permanent magnet fabrication, but to date no magnets have been fabricated from $Sm_2Fe_{17}N_x$. This is because of the chemical instability of the nitride at sintering temperatures.

C. Magnetism of Nitrogenated $La(Co_{1-x}Fe_x)_{13}$ Alloys

Two of the requisites for a useful high energy permanent magnet material are: (1) a high Curie temperature (T_c) and (2) a large magnetic induction, B_r. $La(Co_{1-x}Fe_x)_{13}$ has a T_c of 1045 C (for $x = 0.6$) and a B_r of 20 kG (which accords with a theoretical energy product of 100 MGOe). On the basis of these two features, it is of potential significance as a permanent magnet material. However, it is a cubic material and, as such, it is not expected to exhibit any anisotropy of significance. It is also not expected to display significant coercivity, and this would spell doom for it as a permanent magnet material.

The beneficial effect of nitrogenation on the magnetic behavior of R_2Fe_{17} systems has been alluded to above. The thought occurred that there might be a similar effect with $La(Co_{1-x}Fe_x)_{13}$ alloys; specifically, nitrogenation might degrade the cubic symmetry. Should this happen, anisotropy and coercivity could be developed. The results reported in publication No. 32 indicate that the hoped-for symmetry degradation is not brought on by nitrogenation.

It should be emphasized that the work reported in No. 32 does not close the door on the development of 1:13 type permanent magnets. Other, more promising formulations remain to be tried - for example,

nitrogenated $La_{1-x}Nd_x[Co_{1-y}Fe_y]_{13}$. The attractive feature of the Nd-containing alloy is that Nd is a non-spherical ion, whereas La is a spherical ion. Symmetry degradation is more probable when the rare earth ion is non-spherical than when it is spherical.

One interesting feature of $La(Co_{1-x}Fe_x)_{13}$ alloys is their large magnetization. In these alloys the Fe and Co carry a moment of 2.39 μ_B per 3d atom, which compares favorably with the maximum Fe-Co moment of 2.46 μ_B per 3d atom found in Fe-Co alloys. (This 2.39 μ_B/atom leads to the value of B_r = 20 kG cited above.)

D. Magnetism of Nitrogen Martensite and $Fe_{16}N_2$

Kim and Takahashi in 1972 used[6] ion implantation to insert nitrogen into Fe thin films. They noted two important consequences: (1) a special nitride - namely, $Fe_{16}N_2$ - formed and (2) this nitride had an atomic moment about 30% higher than that of α Fe. The enlarged moment suggested that $Fe_{16}N_2$ might be useful in electromechanical devices. For this use, $Fe_{16}N_2$ was needed in gram quantities instead of the microgram quantities involved in Kim and Takahashi's thin film work. In the ARO project, activities were initiated in mid-1990 to produce $Fe_{16}N_2$ in gram quantities. In the course of this work, nitrogen martensite had to be formed as a precursor of $Fe_{16}N_2$. ($Fe_{16}N_2$ is an ordered form of Fe_8N.) This work is described in considerable detail in Nos. 10, 11 and 12.

Nitrogen martensite was prepared by treating fine Fe powder with NH_3/H_2 gas mixtures at temperatures around 665 C. Upon quenching to a temperature T_q, the γ phase, which had formed at the elevated

temperature, undergoes a martensitic transformation to form nitrogen martensite (or, as it is often designated, α' Fe-N alloy), a tetragonal material. Heat treating this material for 1 to 2 h. at 140 $\pm$ 10 C produced the α'' phase $Fe_{16}N_2$. In the preparation procedure employed, the α' phase was produced along with a considerable amount of γ Fe-N. From x-ray line intensities, the fraction of α' phase present in the mixture was ascertained. Since the γ phase is non-magnetic, the magnetism of the 2-phase mixture was exclusively due to its α' component. Thus, from the known amount of α' present, one readily calculates the α' moment. The α' phase is found to exhibit a room temperature moment of 250 $\pm$ 10 emu/g.

During the 140 C heat treatment, the α' Fe-N alloy is converted into the α'' alloy, i.e., $Fe_{16}N_2$. However, during the formation of $Fe_{16}N_2$, α Fe is also formed. In addition, there is untransformed γ phase. Thus, a three-phase mixture results. Phase analysis was performed by XRD to establish the relative amounts of the γ, α and $Fe_{16}N_2$ present in the mixture. Since the magnetic moment per unit mass is known for the γ and α Fe phases, the moment of $Fe_{16}N_2$ was readily obtained. By this procedure one obtained 280 $\pm$ 10 emu/g for the saturation moment of $Fe_{16}N_2$, corresponding to an Fe moment of 2.88 μ_B/atom.

The experimental Fe moment, 2.88 μ_B, is in excellent agreement with the most recent band structure calculations[7], 2.85 μ_B.

$Fe_{16}N_2$ has a theoretical energy product of ~ 200 MGOe, which makes it an exciting magnetic material. This has not been realized to date because the $Fe_{16}N_2$ obtained to date was formed in the presence of large amounts of γ' Fe-N, which is non-magnetic, and α Fe, which is more weakly magnetic than α'' Fe-N.

As a measure of the intense worldwide interest in Fe_8N and $Fe_{16}N_2$, a special symposium devoted to these two nitrides was held at the 6th joint meeting of Intermag and the MMM Conference which took place in Albuquerque June 20-23, 1994. All participants in the symposium were invited. Paper No. 12 was presented as part of that symposium.

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DEGREES EARNED

None